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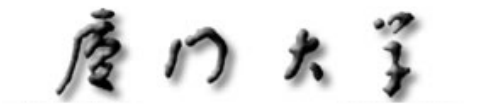

博　士　学　位　论　文

低铂高效燃料电池催化剂的设计与制备

Design and Synthesis of the Low Platinum Loading and High Performance Electrocatalysts for Fuel Cell Application

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Design and Synthesis of the Low Platinum Loading and High Performance Electrocatalysts for Fuel Cell Application

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摘 要

低温燃料电池包括质子交换膜燃料电池、直接醇类燃料电池和直接甲酸燃料电池等，以其不受制于石油和清洁的工作特点成为新能源汽车核心动力部件的代表，它符合我国以煤炭为主要能源资源的国情，燃烧未来的主流燃料甲醇、甲酸和氢气等，大大减轻不堪重负的环境压力。然而，这些燃料电池催化剂均使用价格昂贵、资源稀缺的贵金属铂作为主要活性组分，由此造成的燃料电池成本高昂是制约燃料电池产业化的主因之一。此外，铂作为燃料电池的催化剂还存在容易失活的缺陷。因此，本文围绕燃料电池成本高，反应活性低和稳定性差等制约其商业化的主导因素出发，展示材料的合理设计，通过强化材料的物理和化学性质，寻找可行的新型催化材料路线显得尤为重要。获得的主要结果如下：

首先，通过改进的两相法制备了粒径细小(约2.6 nm)、粒径分布狭窄、组成可控的PtAu合金纳米粒子。将所得纳米粒子组装至碳黑表面并经过热处理后，$Pt_{100-m}Au_m$/C催化剂粒径有所增大，但依然具有很好的单分散性。XRD及计算的晶格常数表明了PtAu双金属的晶格常数与Au的含量显线性关系符合Vegard理论，证实了PtAu具有均相合金性质，该合金相态不同于宏观体系中的不相溶相态规律。该工作的意义是从实验上证明了，在宏观体系中晶格常数差异较大的双金属体系，通过制备工艺的优化可制备新的纳米尺度上的合金。

二、PtAu双金属的尺寸均一，组成可控和均相合金性质为建立双金属组成与催化活性的关系提供了优质的材料基础。在此基础上，以甲酸电催化氧化为探针反应，建立了组成-催化活性的关系，其中催化剂$Pt_{50}Au_{50}$/C的催化活性最优，是商业Pt/C催化剂的8倍，探讨并提出了其催化活性提高的根本原因是体效应的作用，并进一步研究了热处理温度(300~800℃)对$Pt_{50}Au_{50}$/C催化剂的结构性质和催化性能的影响。TEM、XPS和XRD表征表明$Pt_{50}Au_{50}$/C催化剂经低温热处理(300~400℃)后形成合金相态性质，但在高温热处理(如：800℃)则出现相分离现象，Au在颗粒表面富集。电化学测试结果表明甲酸的电氧化活性与催化剂的合金和相分离性质强烈相关。其中经600℃热处理的$Pt_{50}Au_{50}$/C催化剂不仅具有最好的催化活性，是商业Pt/C催化剂的11倍，且具备优异的稳定性能。

三、$Au_{core}@Pt_{cluster}$/C电催化剂上的甲酸氧化行为与Pt的分散度息息相关。具有高Pt分散度的$Au_{core}@Pt_{cluster}$/C在低电位(0.2~0.4 V vs SCE)区域对甲酸电催化氧

化反应展示出很高的催化活性，此时以甲酸直接脱氢氧化生成CO_2的反应为主；但随着Pt分散度逐渐降低时，甲酸电催化氧化反应经由毒性CO中间产物途径变得更加明显，且主要在高电势(0.6~0.8 V vs SCE)区域进行，与商用Pt/C电催化剂上甲酸的电氧化行为极为类似。表明随着Au颗粒表面Pt尺寸的减小或分散度的提高，$Au_{core}@Pt_{cluster}$/C电催化剂对甲酸电氧化反应的催化活性也随之提高。其次，如逐步提高电解质中甲酸的浓度时，在$Au_{core}@Pt_{cluster}$/C（Pt/Au=1/8）催化剂上甲酸的氧化电流呈现先增大后减小的火山形变化趋势。因此，控制甲酸浓度对提高Pt基电催化剂上甲酸电氧化反应的电流密度以及直接甲酸燃料电池的输出功率具有重要的现实意义。

四、在上述基础上提出了催化剂设计和催化的一些新概念与新方法，并基于多组分金属中协同催化和选择性调控的需求，通过置换法设计、合成双金属合金承载超低铂的新型催化剂Pt修饰PdAu/C，XPS 测试的近表面Pt/Pd比例的数值高于实际的投料比例，此外与自制的PdAu/C催化剂相比，CO溶出电化学实验结果表明Pt修饰的PdAu/C催化剂对CO的起始氧化电位及氧化峰电位呈显著的负移，因此以上表征充分印证了在PdAu合金核表面上已生长出铂簇。其中Pt修饰PdAu/C(摩尔比，Pt/Pd=1/100)的电化学活性是商用Pt/C(20%，J-M)催化剂的87倍，这么剧烈的提高表明在超低Pt浓度条件下，表层的Pt原子被有效的孤立进而促进直接氧化途径的发生，抑制毒化物CO的生成，使得体效应更高效的发挥其功能。其次，表层的Pt与内核Pd金属对甲酸都具有脱氢氧化能力，实现了内外双活性中心的设计。因此甲酸电氧化的质量比活性和稳定性得到了大幅提高。

关键词：

燃料电池；超低铂；核壳结构；金铂合金；甲酸电氧化；置换反应

Abstract

Low temperature fuel cells include proton exchange membrane fuel cells (PEMFCs), direct alcohol fuel cells (DAFCs) and direct formic acid fuel cells et al. which utilizing hydrogen、methanol and formic acid et al. as fuels represent an important form of tomorrow's energy. Such energy utilization formats consistence with our country's energy sources supply situation where coal based green productions fuels such as methanol, formic acid, and hydrogen is taking up as majority. However, commercialization of these fuel cells is seriously hindered by the usage of expensive and scare Pt-contained catalysts, which not only led to high cost, but also to the issue of catalyst deactivation and stability for fuel cell applications. Although there were a lot of attempts for non-Pt catalyst for fuel cells, non-Pt catalysts generally have poorer performance than Pt-based. Therefore, it is important to explore a feasible and novel fuel cell catalyst route by improving the chemical and physical properties of these materials against the drawbacks of commercialization due to high cost, sluggish kinetics and long term stability of fuel cell catalysts. The main results in this work can be summarized as follows:

Firstly, a novel strategy for the preparation of a series of carbon supported platinum-gold bimetallic nanoparticles with various bimetallic compositions and high monodispersity was developed based on two-steps method. The PtAu alloy prepared via the method can be well controlled for the composition and nano-size (about 2.6 nm and the narrow size distribution). The as-prepared alloy were loaded onto a carbon black support and subjected subsequently by thermal treatment to become $Pt_{100-m}Au_m/C$, where the alloy particles will increase a bit but stay at well dispersion. The XRD patter and the calculated lattice parameter for the bimetallic nanoparticles were found to scale linearly with the relative Pt/Au content. In other words, they follow a Vegard's law, indicating that the nanoparticles are an alloy rather than a miscibility gap known for the bulk counterpart of the bimetallic PtAu metals. This finding is one of the first examples demonstrating the difference of the physical and

chemical properties for nanoscale materials from the bulk crystalline state.

Secondly, the ability to control the size, composition, phase properties of the $Pt_{100-m}Au_m$/C catalysts enabled us to establish the correlation between the bimetallic composition and the electrocatalytic activity for FA electrooxidation. Within examination of a wide range of bimetallic composition, the $Pt_{50}Au_{50}$/C catalyst shows the highest electrocatalytic activity for the FA oxidation and eight times higher mass activity than that of Pt/C. The high performance of the PtAu/C catalyst can be ascribed to the increased selectivity toward the FA dehydrogenation at the decreased availability of adjacent Pt atoms. The effects of thermal treatment (between 300~800℃) on the structure and catalytic properties $Pt_{50}Au_{50}$/C were also determined. The findings from the XPS and XRD characterizations have provided important information for us to pin down the alloying and phase segregation structures as a function of the thermal treatment temperature. In contrast to the largely alloyed character for the catalysts treated at 300~400℃, the higher-temperature treated catalysts (e.g., 800 ℃) are shown to consist of a Pt-rich alloy core and an Au shell or phase-segregated Au domains enriched on the surface. The electrochemical and electrocatalytic activities are highly dependent on the nanoscale evolution of alloying and phase segregation. The $Pt_{50}Au_{50}$/C catalyst shows the highest electrocatalytic activity（11 times of Pt/C catalyst activity）and stability for the FA oxidation when treated at 600℃.

Thirdly, the electrooxidation behavior of formic acid was greatly influenced by the morphology and dispersion of Pt deposition on the Au nanoparticles. The electro-oxidation of formic acid occurred mainly in the high potential range (0.6~0.8 V vs SCE) when the Pt existed as a low dispersion ($Au_1@Pt_1$/C), which is similar to the electrocatalysis of a Pt/C catalyst. When the state of Pt deposits was a very small flecks of Pt clusters or two dimensional rafts ($Au_8@Pt_1$/C) on the same Au particles, dramatic enhancement in the oxidation current of formic acid was observed in the low potential range (0.2~0.4V vs SCE). These results demonstrate that the catalytic activity of $Au_{core}@Pt_{shell}$/C catalysts for formic acid electrooxidation could be dramatically enhanced by decreasing the size of Pt entities or increasing the Pt

dispersion on Au particles. On varying the concentration of formic acid, we observed distinct volcano curves by correlating the electrooxidation current with the concentration of formic acid for $Au_8@Pt_1/C$ catalysts. Therefore, the determination of an appropriate concentration window for formic acid can be a key factor for the power densities of direct formic acid fuel cells using Pt-based electrocatalysts.

Fourthly, based on the understanding of the formic acid electrooxidation mechanism and ensemble effect, we propose a rational design strategy to the construction of a novel type of catalytic nanostructures (Pt decorated PdAu/C) with nanoengineered surface structures, by means of a well-known spontaneous displacement reaction. XPS results show a higher concentration of Pt on the particle surface in Pt-PdAu/C compared to the norminal atomic ratio of Pt and Pd. Besides, It is noted that the presence of the small amount of Pt induces a subtle decrease in the onset oxidation potential and peak potential for CO-stripping, hinting that the presence of Pt facilitates the electrooxidation of CO_{ads}. The finding supports the assessment that a decorated structure is formed for the Pt-PdAu/C catalyst. The results show that the as-prepared Pt decorated PdAu/C with an optimal Pt:Pd atomic ratio of 1:100 exhibits enhanced electrocatalytic activity for formic acid oxidation compared with PdAu/C and 87 times higher mass activity than that of commercial Pt/C catalysts. In this catalyst, the replacement of the Pd atom layer by Pt atoms, which significantly reduces the presence of the so-called "three neighbouring site" of Pd or Pt atoms in the Pt decorated PdAu/C to efficiently suppress CO formation. Moreover, both the decorated Pt atoms and the Pd substrate play the role of the active sites toward formic acid electrooxidation. As a result, the electrocatalytic activity and stability toward formic acid electrooxidation on Pt decorated Pd nanoparticles (the optimal atomic ratio, Pt : Pd = 1 : 100) is unprecedentedly enhanced.

Keywords:

Fuel Cells; Ultra-low Pt Loading; Gold-Platinum Alloy; Core-Shell Structure; Formic Acid Electrooxidation; Displacement Reaction

第一章 绪论

1.1 引言

能源是整个世界发展和经济增长的最基本的驱动力，是人类赖以生存和发展的基础。煤、石油、天然气等化石能源是现今全球消耗的最主要能源。其中，全球消耗的能源中化石能源占比高达 87%。但随着人类的不断开采，化石能源的紧缺及枯竭是不可避免的。其次，化石能源的使用过程中会新增大量温室气体 CO_2，也会产生一些有污染的烟气，威胁全球生态。20 世纪所建立起来的庞大的能源体系已无法适应未来社会对洁净、高效、经济、安全能源体系的要求，能源发展正面临着巨大的挑战。因此，开发更环保洁净的可再生能源是今后发展的主流[1]。

燃料电池是一种直接、高效的将反应物的化学能转化为电能的发电装置。其中，低温燃料电池如质子交换膜燃料电池(PEMFC)、直接甲醇燃料电池(DMFC)和直接甲酸燃料电池因(DFAFC)具有工作温度低、能量密度和功率密度高、结构简单紧凑、可快速启动、使用和维护方便等优点。它的发电效率受负荷变化影响较小，不仅能为集中或分布式发电装置提供可靠动力(主机组)，国家电网的“调峰”发电机组(辅机组)，也可作为军舰或陆地上市县区交通车辆的动力系统。近年来，众多研究机构将低温燃料电池技术作为开发的重大项目，期望在更广阔的领域里获得大规模应用，包括各种军事或商业用途，其中电动汽车方面的应用被认为是其最重要的用途 [2-5]。

1.2 低温燃料电池的概述

燃料电池是一种直接将燃料中的化学能高效、清洁地转化为电能的电化学发电装置，它具有能量转化效率高、零排放或者低排放、快速启动、噪音小等优点，被公认为 21 世纪能源之星。1839 年，英国科学家格罗夫(Grovel) [6]通过水的电解过程发现了燃料电池的原理，并发表了第一篇关于燃料电池研究的报导。1889 年，蒙德(Mond)和朗格尔(Lange) [7]采用氧气和氢气分别作氧化气和燃气，以 Pt 黑为电催化剂，用浸有电解质的多孔非传导材料作电池隔膜，钻孔的 Pt 或 Au 片为集流极组装出电池，并开始使用“燃料电池”的这一名称。1894 年，奥斯